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DYE DOPED CLAD MODIFIED EVANESCENT OPTICAL FIBER (CMEOF) SENSOR ARRAY FOR THE DETECTION OF AQUEOUS-AMMONIA

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ABSTRACT

We are currently developing pH sensitive dye doped clad modified evanescent optical fiber (CMEOF) sensor array for the detection of aqueous-ammonia. The quasi-distribution of CMEOF ammonia sensors allows efficient measurement of aqueous-ammonia at several locations using a single fiber optic line. CMEOF sensors are fabricated by immobilized pH sensitive dyes in sol-gel and applying the dye doped sol-gel as a thin film around a bare core optical fiber. The CMEOF sensors are then sealed from water using a gas permeable membrane, PDMS-vinyl. The dyes in each CMEOF sensor are tailored to operate at slightly different wavelengths by appropriate choice of dyes. Wavelength-division-multiplexing (WDM) and linear system of equations (LSE) are used to interrogate each CMEOF sensor and determine the concentration of aqueous-ammonia at each sensor location.

INTRODUCTION

The use of optical fiber sensors for chemical detection of containments such as ammonia is currently of great interest in the scientific community and of industry. Environmental awareness of society is steadily increasing as we become more aware of the effects of pollution on our health and on our environment[1]. Methods to efficiently measure the containments and determine the level of concentration are important and can be used by stake holders to make corrective action once dangerous levels are apparent. Optical fiber sensors have great potential in the detection of chemical containments. Optical fibers are immune to electromagnetic noise, capable of high sensitivity, and are relatively inert[2]. In addition, fiber optic sensors can be employed in volatile environments. The current interest in ammonia sensor technology is combining clad modified evanescent optical fiber (CMEOF) sensors with pH sensitive dyes[1,3,4] and a gas permeable membrane such as PDMS[1]. In a CMEOF ammonia sensor, a small section of the cladding is removed and a thin layer of pH sensitive dye immobilized in sol-gel is applied around the core of the fiber[1,3,4]. The gas-permeable membrane (GPM) allows the CMOEF ammonia sensor to operate in the aqueous environment by blocking the water content and permeating the ammonia gas.

Various techniques have been employed in the interrogation of quasi-distributed optical sensors including time domain reflectometry, wavelength-division-multiplexing (WDM), and interferometry[2]. In this research we have developed a two element CMEOF ammonia sensor array interrogated with WDM using dyes that operate at different peak spectra. Specifically, we used Bromocresol Green and Phenol Red dyes operating at 618 nm and 550 nm, respectively. The CMEOF sensors have a GPM layer fabricated from PDMS-vinyl. In addition, the CMEOF sensor array is interrogated using a broadband light source and a UV-visible spectrometer. Techniques such as the solution of linear system of equations (LSE) are employed to extract individual sensor response and determine the concentration of ammonia at each sensor location. The advantages of WDM-LSE technique are lower bandwidth requirements; cross-interferences among sensors are minimized; low cost light-emitting-diodes (LED) and silicon detectors can be used. We will discuss the principle behind the CMEOF ammonia sensor array and describe the fabrication procedures. The absorbance response of the CMEOF sensor array as function of the ammonia concentration is shown. Results show that the CMEOF sensor array response is a composite of individual CMEOF sensor response.

1. AMMONIA SENSOR PROBE

1.1 Ammonia sensing principle

The Ammonia fiber sensor developed is a clad modified evanescent optical fiber (CMEOF) sensor. In a CMEOF sensor

part of the optical fiber clad is removed and replaced with a chemical sensing layer. On top of the sensing layer is a gas permeable membrane (GPM) that blocks water and allows gas to go through the layer. Figure 1 shows a CMEOF sensor. When the light is launch into the core of the optical fiber, the evanescent field will penetrate into the sensing layer. The sensing layer will absorb part of the power in the optical beam (P_{in}) and thereby reduce the overall power in the optical fiber (P_{out}).

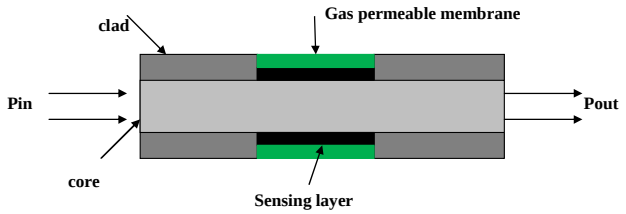


Figure 1. Clad modified evanescent optical (CMEOF) sensor.

The sensing layer in our case is a pH sensitive dye immobilized in sol-gel. The chemical reaction between ammonia and the dye are shown in (1).

$$\begin{aligned} &NH_3(vapor) + H_2O \Leftrightarrow NH_4^+ + OH^- \\ &H\_Dye(orange) + OH^- \Leftrightarrow Dye^-(blue) + H_2O \\ &Dye^-(blue) + NH_4^+ \Leftrightarrow H\_Dye(orange) + NH_3(vapor) \end{aligned} \quad (1)$$

In the first reaction (1), ammonia gas in the water penetrates the gas-permeable membrane and reacts with the small water content trapped in the sensing region producing ammonium ions and hydroxide anions. The de-protonation of the dye by the hydroxide anion results in a color change of the dye. The depth of the color change is directly related to the concentration of the aqueous-ammonia. Once aqueous-ammonia is removed, the ammonium ion protonates the ionized dye, returning the dye to its original state.

1.2 Interrogation of CMEOF sensor array using WDM and linear system of equations (LSE)

The WDM technique is used to interrogate the CMEOF sensor. To use WDM each sensor along the optical fiber operates at different peak wavelengths. An interrogation source operating at the desired sensor operating wavelength can then access the absorption information at the particular sensor position. Ideally, the resulting output should be from the desired CMEOF sensor with low cross-talk and minimum interference with the other CMEOF sensors. If the spacing between the operating wavelengths is wide, cross-talk can potentially be minimized. However, cross-talk and interference are significant for the CMEOF sensor array since the spectra width of the dyes are wide and can potentially overlap.

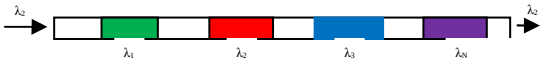


Figure 2. N-element CMEOF sensor array. Each color represents a CMEOF sensor operating at the different peak operating wavelength.

Analytical chemistry techniques such as solution of linear system of equations (LSE) or least square techniques can be employed to untangle complex overlapping spectra. Both processes assume that response of each CMEOF sensor is known beforehand (i.e. calibrated). In this work, we have used LSE and WDM to interrogate and remove the effects of overlapping spectra. For a CMEOF sensor array of n elements as shown in Figure 2, the LSE is given by:

$$\begin{aligned} &A_{\lambda 1} = b^1{}_{\lambda 1}C_1 + b^2{}_{\lambda 1}C_2 + b^3{}_{\lambda 1}C_3 \ldots + b^N{}_{\lambda 1}C_N \\ &\ldots\ldots \\ &A_{\lambda N} = b^1{}_{\lambda N}C_1 + b^2{}_{\lambda N}C_2 + b^3{}_{\lambda N}C_3 \ldots + b^N{}_{\lambda N}C_N \end{aligned} \quad (2)$$

or

$$[b][C] = A$$

where $b_{\lambda i}{}^n$, C_n, and $A_{\lambda i}$ are the response of sensor *n* at wavelength λ, concentration of contaminates at sensor location n, and absorbance at wavelength λ. The sensor response is function of the sensing material absorption coefficient, penetration depth of the evanescent field, and geometric design of the sensor[5]. If the spectra of individual component dyes are completely separable, the matrix **b** will be a diagonal matrix. The response of each CMEOF sensor is determined experimentally in this work and LSE is solved to extract the concentration of aqueous-ammonia at each sensor location.

1.3 CMEOF Ammonia sensor array fabrication

We have developed two component CEMOF ammonia sensor array fabricated from pH sensitive dye immobilized in sol-gel. The CMEOF sensors are bent to increase the evanescent field in the sensing region and thereby increasing the sensitivity of the probe[6]. Figure 3 shows the sensor probe designs for a bent fiber sensor array and Figure 4 shows the fabrication steps conducted. The fiber was fabricated from 105 μm glass optical fiber with 20 μm of cladding. The optical fiber was bent into 3.5 cm diameter loop at two places along the fiber using two plastic tubes as shown in Figure 3. Both ends of the fiber were terminated with SMA connectors. The plastic tubes were then glued in place to the sensor platform.

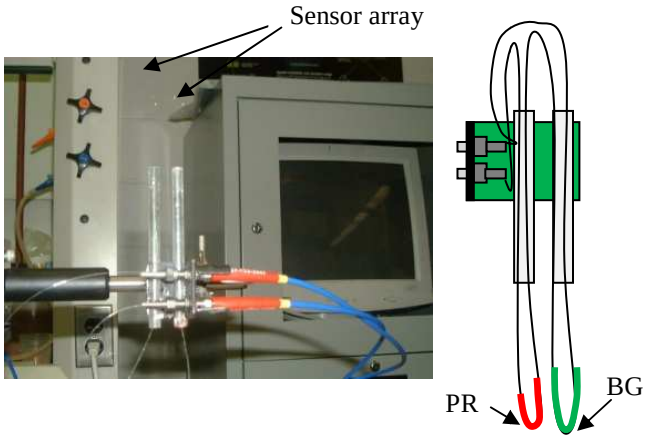


Figure 3. Two CMEOF ammonia sensor array (upright). Left sensor is Phenol Red sensor and right sensor is Bromocresol Green sensor.

A 30% NaOH solution at 240^0 F was then used to etch away ~20 µm of the cladding. The change in optical power through the fiber sensor array was continually monitored using blue LED light source, silicon detector, and signal processing board. The etching was terminated when the optical power in the fiber dropped by 25%. A dipping machine was then used to precisely dip the etched fiber into dye-sol solution. Bromocresol green (BG) and Phenol Red (PR) dye-sol solutions were used. PR has an absorption peak at 550 nm and BG has peak absorption at 618 nm. The dye-sol solutions were prepared by hydrolyzing Tetramethoxysilane (TMOS) using 2 part TMOS and 1 part di-water-dye solution. The procedures to make sol solution have been described previously by Tao[5]. The sensor was then allowed to try for a period 24 hrs. The dye-sol-gel coated fiber was then dipped into a solution of polydimethylsiloxane-vinyl (PDMS-vinyl) to create the gas-permeable layer. The PDMS-vinyl layer was then air cured over a week.

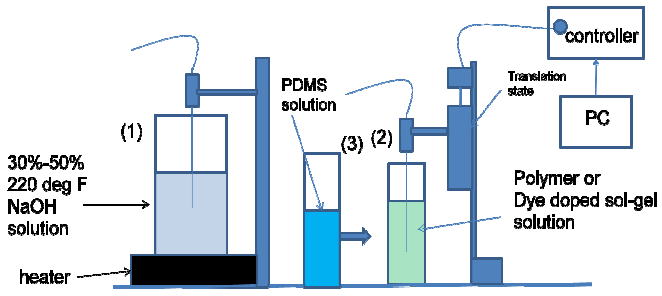


Figure 4. Fabrication process for the dye-immobilized clad modified evanescent ammonia sensor

2. EXPERIMENTS AND RESULTS

The CMEOF sensor array was clamped to a 12" post. The tips of the sensor array were then dipped into 100 mL di-water. A broadband Tungsten source and spectrometer were then connected to CMEOF sensor array using fiber cables. Figure 5 shows the interrogation system for the sensor array. Up to six drops of 15M NH_4OH solution was then added using a dropper and then mixed with the di-water. Spectra measurements were taken 10 minutes after each drop to allow even distribution. Each drop is roughly 40uL and corresponding to a concentration of 100 ppm of NH_3 when added to the 100 mL di-water. This assumes that all the NH^+_4 are converted into dissolved NH_3 gas by the high pH. The pH level was checked by adding small amounts of Phenol Red dye to the di-water.

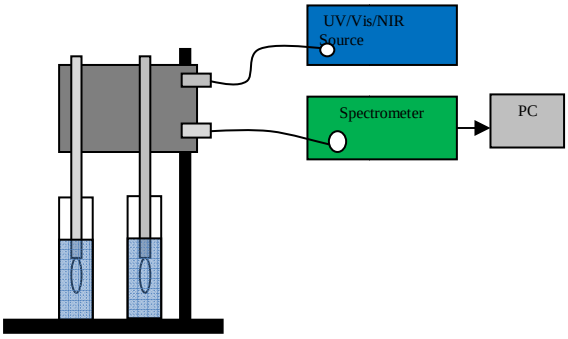
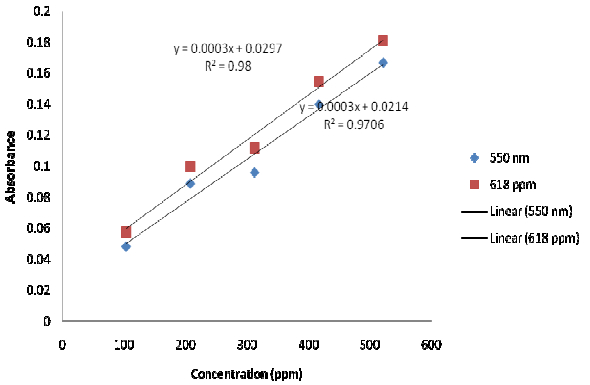


Figure 5. Experimental setup of CMEOF sensor array. A broadband source and a computer controlled spectrometer are used to interrogate the sensors.

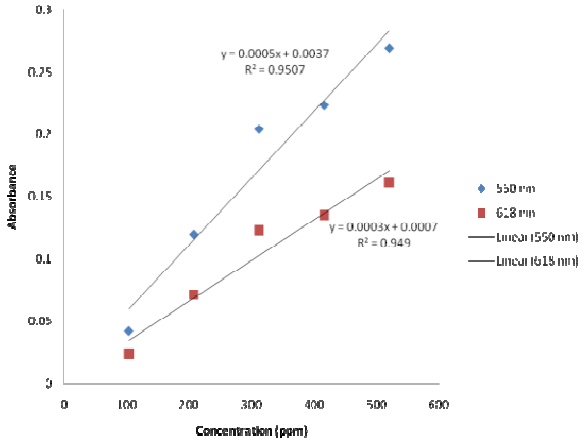
Figure 6 shows the resulting absorbance as a function of the change in concentration of ammonia at 550 nm and 618 nm. Figure 6 (a) shows the case when BG dyed CMEOF sensor is exposed to aqueous-ammonia while the PR dyed CMEOF sensor is kept in pure di-water. Figure 6(b) shows the case when PR dyed CMEOF sensor is exposed to aqueous-ammonia while BG dyed CMEOF sensor is kept in pure di-water. Finally Figure 7, shows the case when both CMEOF sensors are simultaneously exposed to the same concentration of aqueous -ammonia. In all three plots, a linear fit was taken to determine the continuous response of the sensor array as a function of the aqueous-ammonia concentration and absorbance at the operating wavelength of dyes. The slope of the linear fit is the sensor response (b) as given by LSE (2). We can see from the linear fit results that there is significant overlap of the spectra. For the case when the sensors are exposed to the same aqueous-ammonia concentration, the response of CMEOF sensor array at the two operating wavelengths are essentially the sum of individual sensor response as shown in Figures 6(a) and 6(b). This result is also predicted by LSE when the concentrations are made equal ($C=C_1=C_2$). Summing the fitting equations as shown in Figure 6(a) and 6(b), the absorbance of the CMEOF sensor array as a function of the ammonia

concentration at 550 nm and 618 nm as given by the solution of LSE are as follows:

$$A_{618nm} = 0.0006C + 0.0304$$
$$A_{550nm} = 0.0008C + 0.0251 \quad (4)$$



(a)



(b)

Figure 6. Absorbance of CMEOF ammonia sensor array as a function of ammonia concentration when (a) BG CMEOF sensor and (b) PR CMEOF sensor are exposed to aqueous-ammonia.

Compare (4) to the experimental results as given by the linear fitting equations as shown in Figure 7:

$$A_{618nm} = 0.0005C + 0.0055$$
$$A_{550nm} = 0.0007C + 0.009 \quad (5)$$

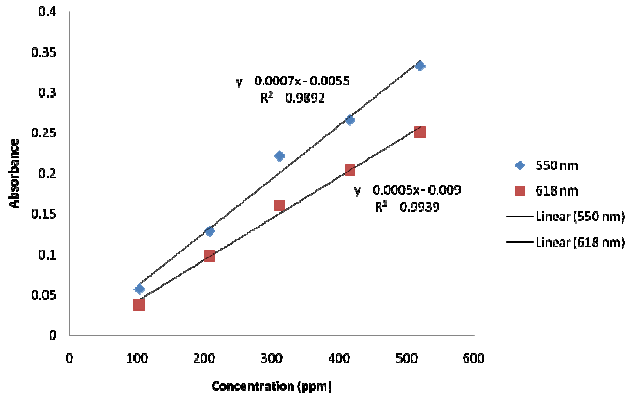


Figure 7. Absorbance of CMEOF ammonia sensor array as a function of aqueous-ammonia concentration when BG and PR CMEOF ammonia sensors are simultaneously exposed to aqueous-ammonia.

Comparing the results as given by (4) and (5), we see that they are off by 12.5% at 550nm and 17% at 618 nm. The rate errors are primarily due to the measurement procedure and hysteresis when the dyes do not fully return to their original state.

During the experiment we constantly moved the sensor array in order to remove and refresh the di-water. The result here are preliminary, we expect to redesign the measurement procedure so as to not move the sensor from the water, possibly using a pump to remove and refresh the di-water. In addition, the errors should reduce when more wavelength positions are added by introducing more sensors or increasing the number of wavelength measurements. This will allow the use of more advanced signal processing techniques such as least square method. In addition, the spectrometer and broadband source will be eliminated and replaced by embedded control system utilizing multi-wavelength LEDs, silicon photo-detectors, and reference fiber. The reference fiber will help reduce measurement errors by taking the variation of the light intensity into account.

3. CONCLUSION

We have developed a two element dye/sol-gel clad modified evanescent optical fiber (CMEOF) ammonia sensor array. The sensor array was employed in the aqueous environment with the aid of gas-permeable membrane. The gas-permeable membrane allowed ammonia gas to flow to sensor while blocking the passage of water. The sensor array was interrogated using wavelength division multiplexing (WDM) by employing two dyes operating at different wavelength. The spectra overlap of the dyes was minimized by solving a system

of linear equations (LSE). The WDM-LSE method reduced cross-interference among the sensors and extracted the concentration of aqueous-ammonia at each sensor location. Sensor responses and absorbance measurements were then taken as function of the concentration of the aqueous-ammonia. The measurement errors were within 17% and the results show that the response of the sensor array is a composite of individual sensor response.

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